Japanese Published Unexamined Patent Application (A) No. 05-148658, published June 15, 1993; Application Filing No. 03-334454, filed November 22, 1991; Inventor(s): Akio Takatsu et al.; Assignee: Sumitamo Metal Mining Corporation; Japanese Title: Electroless Tin-Plating method

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ELECTROLESS TIN-PLATING METHOD

CLAIM(S)

1) An electroless tin-plating method, wherein the electroless tin plating treatment is applied after the surface of an object to be plated is treated with an admixture of acid, peroxide, and of organic high polymer in the process of applying electroless tin plating to a copper.

2) An electroless tin-plating method, as cited in Claim 1, wherein the object to be plated is treated with electroless tin plating, followed by annealing treatment.

3) An electroless tin-plating method, as cited in Claim 1 or Claim 2, wherein a solution containing one type or more out of sulfuric acid, hydrochloric acid, nitric acid, and phosphoric acid is used for said acid.

4) An electroless tin-plating method, as cited in Claim 1 or Claim 2, one of ammonium persulfate and hydrogen peroxide is used for said peroxide.

5) An electroless tin-plating method, as cited in Claim 1 or Claim 2, wherein a chemical compound, in which straight chain hydrocarbon, cyclical carbon compound, or their derivatives are bonded to a sulfuric

group or phosphoric group, is used for said organic high polymer compound.

DETAILED DESCRIPTION OF THE INVENTION

(0001)

(Field of Industrial Application)

The present invention pertains to an electroless tin-plating treatment technology for tape carrier for use in IC chip mounting, particularly to the electroless tin-plating method that can prevent whiskers from being generated on the plated surface after the plating.

(0002)

(Prior Art)

In recent electronics industry, low-cost and highly reliable multi-functional devices are rapidly developed. As highly functional and high density chips emerge in the industry, voices demanding highly reliable, multi-functional, lightweight, thin, and small devices are increasingly raised. In response to these demands, development of a novelty chip-mounting technology is becoming more and more important day by day; particularly, diversification and miniaturization of an IC package are important focuses of said development. Also, along with this advancement

in such a chip-mounting technology, there is rising expectation for the development of a tape carrier having micro distance between pins that can meet the demand for use of more pins in a smaller IC package.

(0003)

TAB refers to a method, whereby multiple ultra fine lead patterns made of bonding metal are formed on an electrically insulated synthetic resin substrate, such as a polyimide resin film in tape form, and the tape is characterized in that its having a test pad makes it easy to find the problems, such as defective bonding or defective chips, after the bonding, and in that it makes it possible to further increase the number of pins despite of the IC pad being small in size, relative to wire boding.

(0004)

At present, a three-layer TAB constructed by bonding a copper foil onto a resin film with an adhesive is in a main stream. This 3-layer TAB, however, comes with a limit in increasing the number of pins, which is indispensable in high density mounting, since its lead is formed by etching. By contrast, a two-layer TAB is advantageous in increasing pins for its lead being formed by electrical plating, but its lead pitch that can be formed largely depends upon the resolution of a resist since an optical technology such as photolithography using a resist is used for forming the lead;

therefore, both TAB methods depend upon an etching technology and a resist technology for the quality and performance.

(0005)

As to the method for mounting the TAB on an IC chip, there is a widely used gag bonding method, whereby the lead of the TAB is overlapped over the preformed bump, which then is put to thermal compression bonding. This method is more efficient than the prior art wire bonding method used for bonding a lead frame. In this respect, it can be said that the TAB is excellent for mounting IC chips.

(0006)

A bump formed on an IC chip is generally made of gold, so it will be most appropriate if the copper lead on the side of TAB is also plated with gold for reinforce the bonding strength but, due to cost factor, tin plating is recently used instead of gold plating. This is due to the fact that tin forms an eutectic with gold, so the eutectic alloy is generated when thermal compression bonding is applied to the tin formed on the lead of the TAB and gold bump of IC chip, reinforcing the sufficiently reliable bonding strength.

(0007)

As to the method for forming the tin-plating film on the copper lead, an electrical tin-plating method or an electroless tin-plating method can be used, but an electroless tin-plating method is generally used rather than an electrical tin-plating method taking into consideration the lead pattern connection and uneven plating thickness.

(0008)

(Problems of the Prior Art to Be Addressed)

Said tin-plating method is one of the useful method as a TAB formation technology for IC mounting in terms of cost and performance but, on the tin-plated film formed on the copper, are often generated needle-shaped protrusions (hereinafter referred to as whiskers) called whiskers in perpendicular direction to the film. These whiskers, once generated, grow with time to so long as to the maximum of some mm order. These whiskers tend to generate in the end section or angular section of the object to be treated. With the TAB, the whiskers mostly generate in the inner lead. With the future mounting technology, the number of pins moves to even higher density, so the inner lead pitch of the TAB is further become ultra fine and is expected to become some tens μm [sic] order [Translator's note: "Some tens" is a phrase unique with Japanese language, which does not find English equivalent; the phrase means "any number between 10 and 90."].

Therefore, this growth of said whiskers may possibly cause a short circuit to be generated in the adjacent leads, which results in a defective end product.

(0009)

At present, there is no proper method for solving the problem of whisker generation. Even though improving the plating solution and a post-treatment after plating are being studied, there is no decisive method found up to now. As a measure to the whisker generation, an annealing method for heating after tin-plating treatment and a method to preserving it at a low temperature are coupled, but both methods are focused on the measure as to how to extend the latent period prior to the whisker generation and have not come up with a fundamental measure to prevent the whisker generation.

(0010)

The present invention, to solve the aforementioned problems, attempts to present an electroless tin-plating method that can completely prevent the whiskers from being generated at a time of applying the electroless tin-plating treatment.

(0011)

(Means to Solve the Problems)

To solve the aforementioned problems, the method of the present invention is characterized in that a copper is used as an object to be plated,

and when electroless plating is applied to this copper, the surface to be plated is treated with an admixture solution of acid, peroxide, and of organic high polymer compound before the electroless plating.

(0012)

Said method also includes a step of annealing said plated object after said surface treatment.

(0013)

As to the acid solution used in the process of electroless tin-plating, a solution containing at least one or more types selected out of sulfuric acid, hydrochloric acid, nitric acid, and phosphoric acid is preferred. As to the peroxide, ammonium persulfate or hydrogen peroxide is preferably used. As to the organic high polymer compounds, a compound or its salt, wherein a straight chain hydrocarbon, or cyclical carbon compound or its derivative is bonded to a sulfuric acid group or phosphoric acid group.

(0014)

(Function)

The present invention is explained below in detail with reference to its function.

(0015)

A theory of electroless thin-plating is that a tin that cannot be intrinsically deposited on a copper due to electrode potential can be deposited on the copper by adding to the plating solution a specific type of compound that can drop the electrode potential of the copper lower than the electrode potential of the tin.

(0016)

As to this type of compound, a thio urea is widely used. Accordingly, the tin is deposited on the copper by a substitution reaction, so it is easily thinkable that the surface condition of the copper, e.g., micro roughness, has an impact on the tin plated on the copper.

(0017)

There are various theories on the reason why the whiskers are generated in the process of tin plating. Up to now, the basic reason is not confirmed, but the most convincing reason is that the whiskers are generated by the residual stress of the copper. Most dominant opinions claim that the most effective and simple method for properly preventing the whisker generation is an annealing method wherein the tin after plated is heated at 90 - 120°C for several hours. This method also supports said residual stress theory. However, even if said heating method is applied, the whisker generation cannot be completed eliminated if it may possibly be prevented.

(0018)

The position where the whiskers tend to be generated is generally the angular section of the lead leading edge of an object having ultra fine circuits, e.g., TAB. Accordingly, it is thinkable that the whisker generation is controlled by the surface condition of an object to be plated on. The fact that the whiskers tend to be generated in the angular section of the lead leading edge is presumably caused by the roughness on the surface of the object to be plated on when viewed microscopically, which implies that the smoother the surface of the object is, the better the whisker generation is prevented. Therefore, it is considered that making the surface of the object smoothest as possible before application of tin plating is a most effective means of prevent the whisker prevention.

(0019)

An object to be plated on is generally cleaned on the surface by a chemical and physical treatment before the plating treatment no matter which wet method is used. This process is generally called pretreatment, the purpose of which is to improve the adhesion of the plated film to the object and its appearance.

(0020)

The operation of pretreatment primarily includes a degreasing process of removing an oil attached to the surface of the object to be plated and an activation process of removing the oxide film formed on the plated surface of the object. For the former process of degreasing, a method using electrolytic decomposition other than a method using an organic solvent is used. For the latter process of activation, a method to remove the oxide film for every material by using a solution capable of dissolving the object plated on, a method to remove the oxide film by using a mineral acid, such as a sulfuric acid or nitric acid, or the combined method of both is generally used.

(0021)

The electroless tin-plating method also uses without exception the aforementioned degreasing process and the activation process as the pretreatment. With the general activation process, however, the oxide film is removed by dissolving the oxide film on the copper surface, i.e., the object to be plated one, so the surface of the copper surface is necessarily roughened after the activation process and before the plating process. This contributes to the acceleration of the whiskers based on the aforementioned theory.

(0022)

In the method of the present invention, the surface of copper after the activation process is successfully smoothed by adding an organic high polymer compound to the activation-processing solution. The probable reason why the copper surface is smoothed by adding an organic high polymer compound to said solution is that the organic high polymer compound present in said solution is adsorbed to the recessed sections in the copper surface and decelerates the dissolution of the oxide in the recessed sections more than the dissolution in the protruded sections. As a result, the microscopic roughness on the copper surface is reduced.

(0023)

As to the structure of the organic high polymer compound having said function, it was found that a preferable one is a compound having both functions of hydrophilic functional group straight chain carbon compound, such as a sulfuric acid group or phosphoric acid group, and hydrophobic functional group, such as a cyclical carbon compound. In the present invention, said organic high polymer compound is actually dissolved in the solution used as a polishing fluid before the activation process is applied, and its concentration is approximately a few % in weight to produce a sufficient effect. As to the processing time, it is not any different from that for a general process wherein the process is applied with the activation

solution not containing the organic high polymer compound, but in actual operation, the processing time is preferably determined after having confirmed the surface condition after the activation process.

(0024)

If the activation process using the mineral acid is continued after the smoothing treatment, the same effect will be produced.

(0025)

It goes without saying that applying the annealing treatment to the substrate at a temperature near 100°C after the electroless tin-plating film formation, the effect of the present invention will be further reinforced.

(0026)

(Embodiment Example)

The present invention is explained with reference to the embodiment example below.

(Embodiment Example 1)

A substrate, in which a 1 μm copper film is formed on the top surface of a 50 μm thick polyimide resin film (Kapton 200H made by Toyo Rayon/Dupont Co.), was prepared. On said substrate, was formed a two-layer TAB, in which a copper wire circuit having a 30 μm lead thickness, a 130 μm lead space width, and a lead width 100 μm is made by using a semi-

additive method of lithography and electric plating. This substrate was used as a test sample.

(0027)

By using the substrate thus prepared as a test sample, the electroless tin plating was conducted by the following steps. As the pretreatment prior to plating, said sample was immersed in Makku Sukurin BEG-306 (Kizai Co.) at 20°C for 20 seconds for degreasing treatment. Subsequently, said sample was washed with purified water for 1 minute, followed by the treatment with an admixture solution of ammonium persulfate 5 g/1, sulfuric acid 20 ml/1, of dodecil sodium sulfate 1g/1 at 20°C for 20 seconds.

(0028)

Subsequently, the sample, after having been washed with purified water for 1 minute, was treated with 10% sulfuric acid in volume percent at 20°C for 20 seconds, and dried.

(0029)

In the electroless tin plating process, the sample was treated with Tinposit LT-34 (Sipray Far East Co.) at 70°C for 5 minutes and washed with purified water for 1 minute. The tin film thus plated was nearly 0.6 μm.

(0030)

The sample thus treated was left in atmospheric air, and the whisker generation status was examined by a metal microscope (magnification 200 times), but even after 60 days, the whisker generation was not found at all.

(Embodiment Example 2)

A two-layer TAB was made as a test sample by the same steps as those in the embodiment example 1.

(0031)

The electroless tin film was plated by using the Chemical polishing solution of embodiment example 1 and the same steps as those in the embodiment example 1, except that the dodecyl sodium sulfate concentration was changed to 0.5 g/1.

(0032)

The whisker generation in this sample was examined by the same method as that in the embodiment example 1, but it was not found at all even after 60 days.

(Embodiment Example 3)

A two-layer TAB was made as a test sample by the same steps as those in the embodiment example 1.

(0033)

The electroless tin film was plated by using the Chemical polishing solution of embodiment example1 and the same steps as those in the embodiment example 1, except that the dodecyl sodium sulfate concentration was changed to 1.5 g/1.

(0034)

The whisker generation in this sample was examined by the same method as that in the embodiment example 1, but it was not found at all even after 60 days.

(Embodiment Example 4)

A two-layer TAB was made as a test sample by the same steps as those in the embodiment example 1.

(0035)

Subsequently, the electroless tin film was plated by using the Chemical polishing solution of embodiment example 1 and the same steps as those in the embodiment example 1, except that disodium 1.5-naphthalene disulfonate with concentration 1 g/1 was used instead of dodecyl sodium sulfate. The whisker generation in this sample was examined by the same method as that in the embodiment example 1, but it was not found at all even after 60 days.

(Embodiment Example 6)

The two-layer TAB test sample having the electroless tin film that was formed by the same steps as those in the embodiment example 1 was put to 100°C annealing treatment for 2 hours. The whisker generation in this annealed sample was examined by the same method as in the embodiment example 1, but it was not found at all even after 180 days.

(0037)

The plated tin film was 0.45 μm thick after the annealing.

(Embodiment Example 7)

A three-layer TAB was made by forming a copper wire circuit with a 35 μm lead thickness, 130 μm lead space width, and 100 μm lead width on one of the surfaces of a 100 μm thick polyimide resin film (Kopilex –S by Ube Kosan Co.) by a subtractive method using lithography and etching, and this three-TAB was used as a test sample.

(0038)

The tin film was formed on said sample by the electroless tin plating method by the same steps as those in the embodiment example 1. Subsequently, the whisker generation in said sample was examined by the same steps as those in the embodiment example 1, but it was not found at all even after 60 days.

(Comparative Example 1)

A two-layer TAB was made by the same steps as in the embodiment example 1 and used as a test sample.

(0039)

The tin film was formed on the sample by the electroless tin plating method by using the Chemical polishing solution of embodiment example 1 and the same steps as those in the embodiment example 1, except that the Chemical polishing solution did not contain dodecyl sodium sulfate. When the whisker generation in this sample was examined by the same method as that in the embodiment example 1, a few whiskers were found after 2 days, and after 14 days, there were many whiskers found that have grown so long that the adjacent whiskers had a short circuit.

(Comparative Example 2)

A two-layer TAB was made by the same steps as those in the embodiment example 1 as a test sample.

(0040)

Said sample was put to electroless tin plating by the following steps. First, as the pretreatment prior to the plating, the sample was immersed in Nuetrclean 7 (Sipray Far East Co.) at 80°C for 90 seconds for degcreasing treatment, and washed with purified water. Subsequently, the sample was treated with BPB-60 (Mitsubishi Gas Chemical Co.) at 20°C for 20 seconds.

Then, after the sample was washed with purified water for 1 minute, it was treated with 10% sulfurice acid in volume percent at 20°C for 20 seconds, and dried.

(0041)

Subsequently, the tin film was formed on the sample by the electroless tin plating method using the same steps as those in the embodiment example 1 and put to the post-process after the plating.

(0042)

When the whisker generation in the sample thus made was examined by the same method as that in the embodiment example 1, the whisker generation was confirmed next day, and in 7 days, many whiskers that have grown long enough to cause the lead to have a short circuit were found.

(Comparison Example 3)

The layer TAB sample having the plated tin film made that was made in the comparative example 1 was put to annealing treatment at 100°C for 2 hours. When the whisker generation in this annealed sample was examined, it was found in 30 days, and in 45 days, the many whiskers grown long enough to cause the lead to have a short circuit were found.

(0043)

The plated tin film after the annealing was 0.45 μm thick.

(0044)

(Advantage of the Invention)

As explained above, the defects in the electrical components, such as a circuit board formed by the substrate plated with a tin film, wherein whiskers are generated when the prior art tin plating method is used, can be prevented conducting the pretreatment prior to tin plating of the present invention. In addition, by applying both the pretreatment and the annealing after the tin plating, the effect of preventing the whisker generation can be further reinforced; therefore, the TAB, for which the pins are increasing, can be mounted with significantly higher reliability.